

## THE DEVELOPMENT OF LASER MICROPYROLYSIS OF COAL MACERALS

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### INTRODUCTION

Since the development of the laser several workers have used its unique characteristics to study the pyrolysis of coal (1-11). The use of a focused laser beam to pyrolyze organic materials offers three advantages. The high degree of localization of surface heating allows the selective pyrolysis of micro components in a heterogeneous material such as the macerals in coal. The species resulting from laser heating are emitted from the heated solid surface with a minimum of interaction with the solid or other pyrolysis products thus increasing the probability of detecting primary structural fragments of the solid rather than products formed as a result of secondary reactions. Pyrolysis conditions can be set where selective bond breakage occurs, such as the rupture of alkyl bridges in coal.

The coupling of laser micropyrolysis with mass spectrometric detection of the emitted species offers a method of structural analysis of nonvolatile organic solids.

### EXPERIMENTAL

The laser micropyrolysis mass spectrometer used in this investigation is an upgraded version of the one used in previous studies (1). The heating source used was a 0.1 J pulsed ruby laser. The laser output was focused by a 2X microscope objective lens onto the surface of a polished coal sample placed in the ionization chamber of a CVC 12-107 time-of-flight mass spectrometer. The area to be pyrolyzed was selected by viewing the surface through the same optical system as used to focus the laser beam. The zone of pyrolysis ranges between 10 and 200  $\mu\text{m}$  in diameter, the size being dependent upon the power setting of the laser. The highly localized heating allows the selective pyrolysis of individual coal macerals to be made.

The pyrolysis products formed by laser heating are ionized by a 500 ns pulse of 18 eV electrons. Mass resolution is accomplished by accelerating the ion packet and measuring the time of flight of the respective ions in the packet over a given distance. The duty cycle of the spectrometer is governed by the flight time of the heaviest ion. For the work with coal, a cycle time of 50  $\mu\text{s}$  was sufficient to scan to mass 400. The major modification of the micropyrolysis mass spectrometer was the replacement of the oscilloscope-photographic recording system with an ultra high speed analog to digital converter (TRW model TDC 1007) coupled to a specially designed cache memory which allows the digitization and storing of 32 sequential spectra over a 1.6 ms period. A major difficulty in analyzing the spectrum produced by a single pulse of a TOF spectrometer is that the small number

of ions produced during a single ionization pulse results in a large statistical variation in peak intensity between spectra of the same material whether they are taken successively or in different experiments. By taking a suite of 32 sequential spectra, computer averaging can be used to greatly improve the reproducibility of the spectra. For the analysis of coal pyrolysis products it was found that the optimum results were obtained when the acquisition of spectra commenced after the laser pulse. During the period of laser irradiation there is extensive fragmentation of the products due to their interaction with the laser beam. For a period of approximately 2 ms after the laser is extinguished pyrolysis products can be detected, by recording spectra during this period analysis is confined to those species being emitted from a hot coal surface.

## RESULTS AND DISCUSSION

The spectra for the suite of coals listed in table 1 are shown in figures 1a and 1b. Several factors are discerned in the examination of the spectra. The resolution of a mass spectrum is not sufficient to give unit mass resolution, what is detected is a series of mass clusters. These clusters are numbered from 1 to 15 with the number being equivalent to the number of carbon or carbon plus oxygen atoms that characterize the species contained in a given cluster. Table 2 lists some of the most likely species that would account for each mass cluster.

There is a high degree of similarity between the pyrolysis spectra of the different coals, the major difference being the relative intensities and shapes of the mass clusters. Analysis of these variables reveals several rank related trends. Each mass cluster encompasses a mass range. The location of the cluster is determined by the number of carbon or carbon plus oxygen atoms in the pyrolysis fragments, while the width of the cluster is determined by the distribution of species of varying degrees of hydrogen saturation plus the occurrence of oxygen containing species. These characteristics can be seen by examination of the dashed lines on figures 1a and 1b which are drawn at mass positions 78 and 128, these masses represent one ring and two ring aromatic species, benzene and naphthalene. Both clusters 6 and 10 overlap these mass lines, ion intensity on the high mass side of the line is an indication of hydroaromaticity, the overlap on the high mass side of the mass 128 line is greater than that of the 78 mass line indicating that hydronaphthalene derived species are more prevalent than cyclohexane derived species. It can also be seen that the high mass overlap increases as rank decreases and the H/C ratio increases. The overlap of the clusters on the low mass side is indicative of the free radical nature of the pyrolysis products. There is a general trend of an increase in cluster width to height ratio as the rank of the coal decreases and the H/C and O/C ratios increase.

The aromaticity of the pyrolysis products can be determined by examination of mass clusters 6 and greater. For comparison the aromatic mass region can be divided into two families. The first, clusters 6,7,8 and 9, consists of single ring species plus single ring species with 1,2 and 3 substituent groups, the second family, clusters 10,11,12 and 13, comprises the same pattern for two ring species. Examination of these families reveals that alkyl and hydroxy substituted ring structures are more prevalent than unsubstituted ring structures, i.e., clusters 7,8,9,6 and 11,12,13 > 10. A trend with rank is seen with the shift of the major cluster in the two ring family. In the higher rank coals, those with a vitrinite reflectivity greater than 0.7 percent, disubstituted species, cluster 12, dominate the two ring region. For the lower rank coals, those with a vitrinite reflectivity less than 0.7 percent, trisubstituted products, cluster 13, are the major group in the region. This trend in a shift of the major cluster to products with a higher degree of substitution as rank decreases is found as well in the single ring family. The distribution of clusters in these two families indicates that the

process of laser pyrolysis is selective in bond breakage. Bond rupture occurs predominately at the weaker aliphatic linkages as evidenced in the much greater abundance of di- and tri- substituted products. The stronger aryl-alkyl bond results in a much lower concentration of mono- and unsubstituted ring fragments where at least one aryl-alkyl bond would have to be broken.

Another trend that can be observed in the high mass region is the appearance and increasing intensity of clusters 14 and 15 as rank decreases, the increase of the H/C and O/C ratios with decreasing rank results in a higher probability of finding ring structures with substituent groups. Although cluster 14 would be the first possible occurrence of three ring structures the fact that unsubstituted one and two ring pyrolysis fragments have lower concentrations than their substituted products would lend support to the conclusion that clusters 14 and 15 are predominately highly substituted two ring species. For the case of the lowest ranked coals the relative intensity of the high mass fragments rapidly diminishes leaving one ring structures as the major species.

Further information can be derived from the lower molecular weight clusters. Cluster 1 is due to water, it is interesting to note that methane or methyl groups are not a major product resulting from laser pyrolysis. Cluster 2 is dominated by carbon monoxide and nitrogen, species present as background gases in the mass spectrometer in addition to being generated by the pyrolysis process. Aliphatic fragments resulting from coal pyrolysis can be seen in clusters 3,4,5 and part of 6. Cluster 3 shows a bimodal distribution in many of the spectra. The low mass peak of this cluster corresponds to potassium, mass 39, under conditions of laser heating potassium is thermally ionized, greatly increasing its detection sensitivity (12). The major fragment ions for the C3-C6 alkane series would appear at masses 43, 57, 71 and 85, clusters 3, 4, 5 and 6. For each of these clusters there is little evidence of the presence of these ions, the mass of major intensity for each of these mass clusters is lower by 2-4 mass units indicating that the alkyl fragments are hydrogen deficient. This hydrogen deficiency indicates that the species detected tend to be unsaturated. In addition, it is likely that thermally generated free radical fragments of the pyrolysis process are being detected. Additional evidence for the detection of free radical species can be seen at mass locations 78 and 128, the dashed lines on figures 1a and 1b. At the low ionization potentials used to obtain these spectra the major ion peak for benzene and naphthalene would be their molecular ion at mass 78 and 128 respectively. However in the coal pyrolysis spectra the peaks associated with these species appears on the low mass side of these assignments indicating that benzyl and naphthyl free radicals are being detected. The most likely origin of the low molecular weight hydrocarbon clusters is from alkyl aromatic linkages and the fragmentation of hydroaromatic structures.

## CONCLUSION

Under the conditions used for laser micropyrolysis of coal, primary products including free radical species emanating from a heated coal surface can be detected. By minimizing secondary condensation or cracking reactions the complexity of coal pyrolysis product analysis is greatly reduced. The pyrolysis mass spectra of the vitrinite portion of a series of coals has shown that as the degree of coalification changes there is a continuous variation in the relative distribution of a small number of primary coal pyrolysis products. These pyrolysis products tend to indicate that the primitive structures found in coal consist mostly of one and two ring aromatic and hydroaromatic groups linked by short aliphatic bridges.

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TABLE 1

## COAL SAMPLES

PSOC #	Rank	Province	Region	% RO *	% C (dmf)	% O (dmf)	% Vit (dmf)
263	MVB	Rocky Mountain	Uinta	1.44	90.4	2.2	93
12	HVA	Eastern	Appalachian	0.90	85.5	6.9	47
337	HVA	Eastern	Appalachian	0.89	86.1	5.8	75
1142	HVA	Eastern	Appalachian	0.88	85.9	6.3	87
505	HVA	Rocky Mountain	Uinta	0.75	83.5	8.7	86
330	HVB	Eastern	Appalachian	0.76	83.4	5.4	84
401	HVA	Interior	Western	0.73	82.5	7.9	88
461	HVA	Rocky Mountain	Uinta	0.68	82.5	10.1	88
235	HVB	Rocky Mountain	Uinta	0.68	81.0	11.2	87
854	HVB	Rocky Mountain	Uinta	0.67	81.6	10.6	93
1113	HVB	Rocky Mountain	Uinta	0.59	79.4	12.8	82
437	HVA	Rocky Mountain	Uinta	0.56	80.2	11.8	92
453	HVA	Rocky Mountain	Uinta	0.52	81.2	10.9	88
457	HVB	Rocky Mountain	Uinta	0.52	80.2	11.9	96
500	HVB	Rocky Mountain	Uinta	0.58	80.8	11.2	92
232	HVC	Rocky Mountain	Green River	0.55	77.4	15.3	89

TABLE 2  
CHEMICAL ASSIGNMENTS FOR MASS CLUSTERS

<u>Cluster #</u>	<u>Mass Range</u> <u>m/z to m/z</u>	<u>Chemical Identification</u>
1	15 -- 18	CH <sub>3</sub> , CH <sub>4</sub> , and H <sub>2</sub> O
2	28 -- 34	C <sub>2</sub> alkanes and alkenes, N <sub>2</sub> , CO, CO <sub>2</sub> , and H <sub>2</sub> S
3	39 -- 44	C <sub>3</sub> alkanes and alkenes, K <sup>+</sup> , and CO <sub>2</sub>
4	55 -- 58	C <sub>4</sub> alkanes and alkenes, and ketones
5	65 -- 72	C <sub>5</sub> alkanes and alkenes, and dienes
6	77 -- 86	C <sub>6</sub> alkanes, cycloalkanes, alkenes and benzene
7	91 -- 96	Methyl benzenes, phenols and cycloalkenes
8	105 -- 110	Dimethyl, hydroxy methyl and dihydroxy benzenes
9	119 -- 124	Alkyl and hydroxy-alkyl benzene and indans
10	128 -- 134	Naphthalene, hydroxy-alkyl benzene and dihydronaphthalene
11	141 -- 146	Methyl and hydroxy naphthalene and cycloalkanes
12	155 -- 160	Alkyl and hydroxy-alkyl naphthalenes and tetralins
13	166 -- 172	Alkyl and hydroxy-alkyl naphthalenes and fluorenes
14	178 -- 186	Phenanthrenes, anthracenes and alkyl naphthalenes
15	192 -- 196	Alkyl phenanthrenes and anthracenes

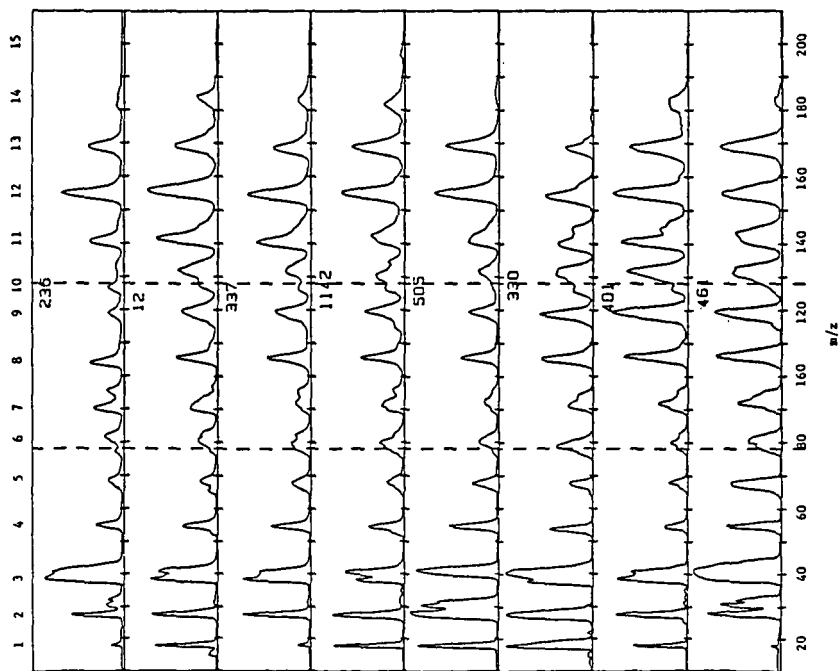


Figure 1a. Averaged Vitrinite Spectra

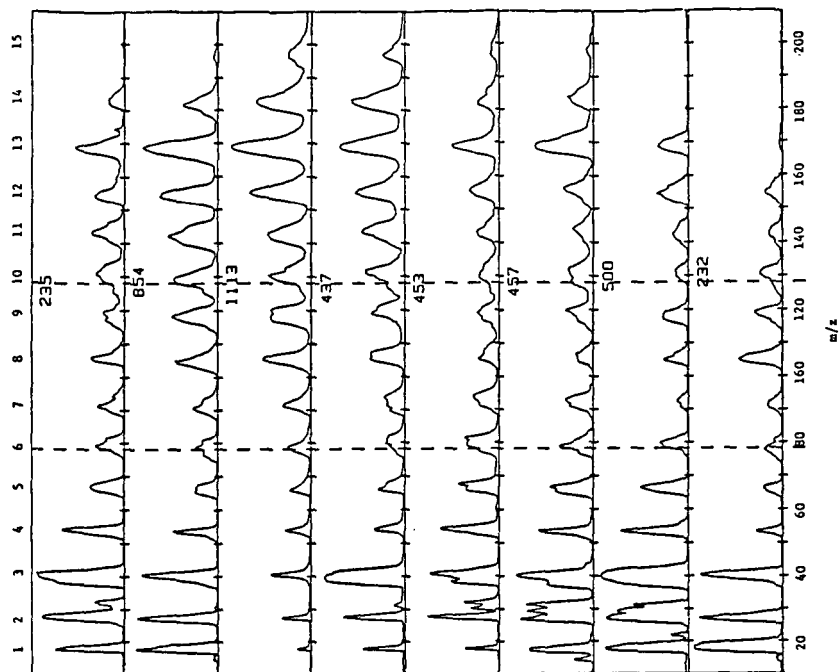


Figure 1b. Averaged Vitrinite Spectra